

Specification

Gas Generant Composition5 **Technical Field**

The present invention relates to a gas generant composition suitable for use in a gas generator for a occupant restraint system, such as an airbag and a pretensioner, used to protect occupants in an automobile from a motor vehicle collision and the like. More particularly, the present invention

10 relates to a gas generant composition for producing burning characteristics suitable as the gas generant.

Background Art

An airbag system, which is one of occupant restraint systems, has been widely adopted in recent years to improve safety of occupants in an

15 automobile. The airbag system operates on the principle that a gas generator is operated under control of signals from sensors detecting a collision, to inflate an airbag so as to cushion the shock of the occupants from the collision. The gas generator is required to have the capability of producing a required and sufficient amount of clean gas containing no

20 harmful substance within a desired time.

In recent years, as the substitution of metallic compound azides that have been used hitherto, gas generants containing organic compounds including nitrogen as fuel components, combined with inorganic oxidizing agents, have been proposed. These known gas generants have the

advantages of generating a large amount of gas and of being less in danger in the manufacturing process. However, many of the gas generators using the organic compounds containing nitrogen as fuel have the heat of combustion as high as 2,500J/g or more and thus the gas generated becomes

- 5 high in temperature and pressure, so that there is a need for the gas generator to have a lot of coolants or cooling media. In addition to this, a slag or a by-product made in the burning of the gas generators is high in temperature and thus in flowability, so that there is a possibility that the slag may flow out of the gas generator and, if the worst happens, may scald
- 10 the occupants. Although any gas generators can be allowed to be improved by using a lot of coolants or cooling media, they are increased in size, going against the trend toward the size reduction and weight reduction of the gas generator.

To solve this problem, there were proposed several methods for

- 15 forming a slag that exhibits a high viscosity even in a high temperature by adding a slag forming agent, for improvement of the slag collecting efficiency. Among others, Japanese Laid-open (Unexamined) Patent Publication No. Hei 4(1992)-265292 discloses the method in which a low-temperature slag-forming agent as typified by silicon dioxide and a high-temperature
- 20 slag-temperature forming agent which produces a solid having a melting point close to or more than the combustion temperature are both added to improve the slag collecting efficiency. However, the slag forming agent itself is little contributive to the generation of gas and, with an increase of the amount of slag forming agent added, the amount of gas generated

decreases. In addition, an increase of the amount of slag forming agent added causes a decrease in combustion speed, thus making it difficult to adjust the combustion speed of the gas generants.

On the other hand, the gas generants arranged in the gas generator
5 are formed into a specified shape, in order to produce a controlled
combustion stabilization of the gas generants and a controlled burning
behavior of the gas generated at the combustion. The combustion speed of
the gas generants varies depending on the constituent ingredients of the gas
generant composition and the particle diameter of the molded products of
10 the gas generants. For the gas generant of slow combustion speed, the
molded products of the gas generants are decreased in unit form or
increased in total superficial area so that the gas can be generated rapidly
within a short time. On the other hand, for the gas generant of rapid
combustion speed, the molded products of the gas generants are increased in
15 unit form or decreased in total superficial area so that a desired gas
generating behavior can be produced.

The burning characteristics of the gas generator are almost always
determined by the burning behavior of the gas generants used. The
burning characteristics of the gas generator are generally evaluated, for
20 example, by a curve plotted between a tank internal pressure obtained by
operating the gas generator in a 60 liter tank and time. In recent years,
the so-called depower technique of protecting the occupants from possible
harm at the inflation of the airbag has attracted public attention. For this
purpose, the gas generator is now being desired to have such burning

characteristics that in the 60 liter tank test of the gas generator, the gas generation speed increases slowly in the period of 10-20 milliseconds from the ignition and then increases sharply on and after 20 milliseconds. The gas generator having this burning characteristic controls the gas generation

- 5 speed moderately at the initial stage of the combustion, to provide a more ideal occupant protecting performance. The burning behavior of the gas generants can be partly controlled by changing configuration or form of the molded products of the gas generants and calculating the amount of gas generated. The relationship between the form of the molded products of
10 the gas generants and the amount of gas generated is an old public knowledge in the field of propellant. For example, a suitable form of the molded products of the gas generants can easily determined by making reference to Explosive Handbook at page 279 (issued from Kyoritsu Shuppan Co., Ltd., 1987), for example.

- 15 Another available methods have been proposed in which at least two gas generant compositions of different combustion speeds are combined in layers so that the burning behavior can be controlled in stages. For example, Japanese Laid-open (Unexamined) Patent Publication No. Hei 6(1994)-48880 discloses the control of the burning characteristics of the gas
20 generator by using this method. Also, Japanese Laid-open (Unexamined) Patent Publications No. Hei 6(1994)-107108 and No. Hei 6(1994)-107109 disclose the gas generants each having a coat of an inert combustion delay on a part thereof. Both of them disclose that the gas generant compositions of different combustion speeds are combined in layers to form the molded

products of the gas generants. When these gas generants are ignited, they are allowed to start burning from a relatively flame retardant layer and thereby the gas generating speed at the initial stage of the 60 liter tank test is suppressed. These gas generants require more processes for the molding
5 than usual, because the gas generant compositions of different combustion speeds are combined in layers. Also, since at least two gas generant compositions are required, the gas generants are manufactured at considerable cost.

- Further, Japanese Laid-open (Unexamined) Patent Publications No.
10 Hei 10(1998)-87390 and No. Hei 10(1998)-324588 disclose the molded products of the gas generants formed into a specified form. These disclose that the gas generants are formed into a specific form, such that as the combustion of the gas generants proceeds, their combustion superficial areas are narrowed at a slowest possible speed, or would rather be enlarged,
15 whereby a desired combustion performance is tried to be produced. However, the both forms of the molded products of the gas generants have a single-hole or multi-hole (porous) tubular form and thus have cavities therein, so that when the gas generants are filled in the gas generator, the filling density is decreased. In addition, since the forms of the gas
20 generants are limited to some specific forms, it is difficult to vary the forms of the gas generants in corresponding to various forms of the gas generators.

It is the object of the present invention to provide a gas generant composition, suitable for use in a gas generator for an automobile occupant restraint system, such as an airbag and a pretensioner, which exhibits the

burning characteristics to produce a further ideal occupant protecting performance, without any complex production process being required for forming the molded products of the gas generants and without any limitation being imposed on the forms of the molded products of the gas
5 generants.

Disclosure of the Invention

The inventors have been devoted themselves to consider possible ways of solving the problems above and found that the burning behavior of the
10 gas generant was improved by defining the composition of the gas generant and have derived the present invention therefrom.

A gas generant composition of the present invention is characterized in that it comprises a fuel, an oxidizing agent and an additive, wherein the fuel comprises at least one high-energy nitrogen-containing organic compound
15 and at least one low-energy nitrogen-containing organic compound, and the low-energy nitrogen-containing organic compound has a 50% average particle diameter of $40 \mu\text{m}$ or less.

The combustion speed of the fuel depends heavily on the reactivity of the oxidizing agent used and the combustion speed. In the present
20 invention, the importance of the combustion speed of the fuel was recognized for the sake of argument of the combustion speed, and a nitrogen-containing compound of high combustion speed was defined as a high-energy nitrogen-containing organic compound and a nitrogen-containing compound of low combustion speed was defined as a

low-energy nitrogen-containing organic compound.

Usually, when two or more different kinds of fuels are used as the fuel of the gas generant composition, the combustion speed does not exceed any combustion speed of the gas generant composition comprising single kind of

- 5 fuel but stands at a nearly constant value of a generally intermediate level between their respective combustion speeds. However, when making a great difference between the energies the fuels have, the gas generant comprising such gas generant composition does not burn at a constant combustion speed. The combustion speed decreases at an initial stage in
10 the form of the combustion of the high-energy fuel being inhibited by the low-energy fuel in a period from the ignition in the gas generator. As a result, the internal pressure of the gas generator fully increases and the combustion speed of the gas generant increases.

When the low-energy nitrogen-containing organic compound has the
15 50% average particle diameter of $40 \mu\text{m}$ or less, or preferably $20 \mu\text{m}$ or less, as in the present invention, the combustion inhibiting effect of the high-energy fuel by the low-energy fuel is produced moderately.

It is to be noted that the 50% average particle diameter of number of reference is a measurement by which a size distribution is expressed on the

- 20 basis of number: when the total number of particles is taken as 100, the particle size obtained when the particles integrated from the smaller number reach 50 is called the 50% average particle diameter of number of reference.

In the 60 liter tank test, the gas generant comprising only the gas

generant composition of the present invention exhibits the burning behavior that it burns at a low combustion speed at the initial stage and then burns at an increased combustion speed. Thus, the gas generant comprising only the gas generant composition of the present invention burns at a varied

5 speed, not at a generally constant speed. In contrast, the conventional gas generant comprising only one gas generant composition burns at a generally constant speed. Hence, the gas generant comprising only the gas generant composition of the present invention is fundamentally different from the conventional gas generant in this point.

10 Thus, the present invention can produce the desired burning behavior without any particular process, such as the process that two or more gas generant compositions of different combustion speeds are combined in layers to form the molded products of the gas generants or the process that the molded products of the gas generants are limited to some specific form, 15 being required for obtaining the gas generant suitable for the gas generator for the automobile occupant restraint system such as the airbag.

 In general, the gas generant composition is selected from the gas generant compositions whose combustion speed can be given approximation to a generally constant combustion speed in the actual operation pressure 20 range of the gas generator. This is because, if a gas generant composition whose combustion speed overly depends on pressure is selected, the combustion speed is varied considerably by an environmental temperature change or a pressure change in the gas generator caused by degradation of the gas generants and the like, so that such a gas generant composition is

not desirable as the gas generant composition used for the gas generator for the automobile occupant restraint system such as the airbag.

The dependency of the combustion speed on the pressure is obtained by a pressure exponent of the following general formula on the combustion speed of explosives. The burning behavior originating from the form of the gas generant can be determined by primarily approximating the gas generating speed, from which the combustion performance of the gas generator can be approximately estimated:

$$V=aP^n \quad (\text{Vieille formula})$$

where "V" is a combustion speed; "a" is an exponent dependent on the composition and temperature; "P" is a pressure; and "n" is a pressure exponent.

It is preferable that a gas generant composition of relative low in pressure exponent and small in variation of combustion speed by the pressure in the general formula above has little dependency of the combustion speed on the pressure and thus is suitable as the gas generant composition used for the gas generator for the automobile riser restraint system such as the airbag.

The gas generant composition of the present invention exhibits the pressure exponent substantially equal to that of the conventional gas generant composition.

Brief Description of the Drawings

FIG. 1 is a schematic view of a gas generator 1 for an airbag used in respective embodiments of the present invention;

FIG. 2 is a graph showing the 60 liter tank test results; and

FIG. 3 is a table showing the 60 liter tank test results.

Best Mode for Carrying out the Invention

A composition of a gas generant of the present invention comprises a
5 fuel, an oxidizing agent and an additive. The fuel comprises at least one
nitrogen-containing organic compound combustible at a high combustion
speed and at least one nitrogen-containing organic compound combustible at
a low combustion speed.

In other words, the fuel of the gas generant composition of the present
10 invention comprises at least one high-energy nitrogen-containing organic
compound and at least one low-energy nitrogen-containing organic
compound. Further, the low-energy nitrogen-containing organic compound
has a 50% average particle diameter of $40\mu\text{m}$ or less, or preferably $20\mu\text{m}$
or less.

15 The gas generator using the gas generants comprising the gas
generant composition of the present invention has such burning
characteristics that in the combustion curve obtained by the 60 liter tank
test, the combustion speed increases slowly in the period of before 20ms
from the ignition and then increases sharply on and after 20ms. The gas
20 generant composition of the present invention exhibits the pressure
exponent of substantially the same level as that of the conventional gas
generant composition. Thus, the use of the gas generant composition of the
present invention to the gas generator can produce an ideal burning
characteristic.

A further detailed description on the gas generant composition of the present invention will be given below.

The high-energy nitrogen-containing organic compound used in the present invention is the compound which is high in enthalpy of formation,

- 5 relatively easy to combust and exhibits a rapid combustion speed. The high-energy nitrogen-containing organic compounds that may be used include those having the enthalpy of formation of -200kJ/mol or more (standard condition), or preferably -100kJ/mol or more. Specifically, at least one high-energy nitrogen-containing organic compound selected from
- 10 the group consisting of aminotetrazole, nitroguanidine, and triaminoguanidine nitrate can be cited as the concrete example of the high-energy nitrogen-containing organic compound.

The low-energy nitrogen-containing organic compound used in the present invention is the compound which is low in enthalpy of formation,

- 15 difficult to ignite and exhibits a slow combustion speed. The low-energy nitrogen-containing organic compounds that may be used include those having the enthalpy of formation of -200kJ/mol or less (standard condition), or preferably -300kJ/mol or more. Specifically, guanidine nitrate and oxamide can be cited as the concrete example as the low-energy
- 20 nitrogen-containing organic compound.

Although the present invention puts no limitation on the combination of the high-energy nitrogen-containing organic compound and the low-energy nitrogen-containing organic compound, the difference in enthalpy of formation therebetween is preferably 200kJ/mol or more.

Aminotetrazole is of preferable as the high-energy nitrogen-containing organic compound in that it contains a high proportion of nitrogen and is relatively high in safety in the handling. Nitroguanidine is also preferable as the high-energy nitrogen-containing organic compound in that it is large

5 in number of moles of the generated gas.

Guanidine nitrate is preferable as the low-energy nitrogen-containing organic compound in that it is relatively available and low in cost, though it is seldom used for the gas generator in that it usually burns at a slow combustion speed when singularly combined with oxidizing agent.

- 10 When aminotetrazole is used as the high-energy nitrogen-containing organic compound and guanidine nitrate is used as the low-energy nitrogen-containing organic compound, the difference in enthalpy of formation is 598kJ/mol. When nitroguanidine is used as the high-energy nitrogen-containing organic compound and also guanidine nitrate is used as
- 15 the low-energy nitrogen-containing organic compound, the difference in enthalpy of formation is 296kJ/mol.

Mixing ratios between the high-energy nitrogen-containing organic compound and the low-energy nitrogen-containing organic compound are between 10:1 and 1:10, or preferably between 5:1 and 1:5 in a ratio of weight.

- 20 The content of the high-energy nitrogen-containing organic compound and the low-energy nitrogen-containing organic compound as the fuel to the total gas generant composition is 15-85 weight%.

Further, when aminotetrazole is used as the high-energy nitrogen-containing organic compound and guanidine nitrate is used as the

low-energy nitrogen-containing organic compound, the mixing ratios therebetween are preferably between 3:1 and 1:3 in the ratio of weight. When nitroguanidine is used as the high-energy nitrogen-containing organic compound and guanidine nitrate is used as the low-energy

5 nitrogen-containing organic compound, the mixing ratios therebetween are preferably between 5:1 and 1:1 in the ratio of weight. When an amount of nitroguanidine is excessive, the combustion speed is significantly decreased. On the other hand, when an amount of nitroguanidine is too little, an adequate combustion performance is not obtained.

10 It is preferable that the low-energy nitrogen-containing organic compound has the 50% average particle diameter of $40\mu\text{m}$ or less, or preferably $20\mu\text{m}$ or less. In fact, as the low-energy nitrogen-containing organic compound decreases in 50% average particle diameter, the combustion speed decreases in the period of before 20ms from the ignition of

15 the gas generant composition. It is noted that it is difficult to pulverize the low-energy nitrogen-containing organic compound, nitroguanidine, in particular, and there have been no reported cases of nitroguanidine being pulverized to $40\mu\text{m}$ or less for use as the gas generant. With the 50% average particle diameter of not less than $40\mu\text{m}$, the effect of the

20 low-energy fuel cannot be provided, so that a sufficient decrease in combustion speed is not provided at an early stage of the combustion.

Further, sufficient collapse strength is not obtained in the press molding of the gas generant composition. With the 50% average particle diameter of $5\mu\text{m}$ or less, the pulverization undesirably requires a

considerable cost, though the effect of the invention can be provided. It should be noted further that since the guanidine nitrate pulverized to 40 μm or less serves as an adhesive agent in the press mold of the gas generant composition of the present invention, the pellets of the gas
5 generant composition produced can have high collapse strength (high hardness).

The oxidizing agents that may be used in the present invention include oxyacid salts, such as nitrate, halogen acid salt and chromate, oxides, and peroxides. Any oxidizing agents may be used, as long as they can oxidize
10 the fuel comprising the high-energy nitrogen-containing organic compound and the low-energy nitrogen-containing organic compound. Preferably, at least one material selected from the group consisting of nitrate, perchlorate, chlorate as concerns alkali metals or alkali earth metals and basic copper nitrate is used as the oxidizing agent. In addition, at least one material
15 selected from the group consisting of mixtures of phase stabilized ammonium nitrate or ammonium perchlorate and nitrate, perchlorate, chlorate as concerns alkali metals or alkali earth metals and basic copper nitrate may also preferably be used as the oxidizing agent. Strontium nitrate that is converted into a high-viscosity, slag-forming metal component
20 by burning is further preferable.

The content of the oxidizing agent can be determined within the range of nearly equivalent within which the gas generant composition is completely burnt stoichiometrically. In the gas generant composition containing the oxidizing agent largely deviating from such an equivalent,

CO or NOx in the combustion gas are significantly increased. The content of the oxidizing agent to the total gas generant composition can be

determined from the range of 30 weight% to 70 weight%. With the content of the oxidizing agent of less than 30 weight%, there is the possibility that

- 5 oxygen supply may fall short so that imperfect combustion may be caused to produce a harmful CO gas. On the other hand, with the content of the oxidizing agent in excess of 70 weight%, there is the possibility that the required gas for the inflation of the airbag may not be supplied.

Strontium nitrate, which is preferably used as the oxidizing agent in
10 the present invention, can be used by itself or in the form of a mixed oxidizing agent by combining with alkali metal nitrate, ammonium perchlorate or basic copper nitrate. To give actual examples, combination of strontium nitrate and potassium nitrate, combination of strontium nitrate and ammonium perchlorate, or combination of strontium nitrate and
15 basic copper nitrate can be cited.

The mixed oxidizing agent in the gas generant composition of the present invention can allow the combustion speed to increase, to provide a harmless combustion gas by adding a small amount of nitrate of the alkali metal and basic copper nitrate. Ammonium perchlorate is particularly

- 20 suitable as the gas generant composition used for the pretensioner, because a small amount of ammonium perchlorate added can produce an increased number of moles of the generated gas by the gas generant.

When potassium nitrate is added, particular attention should be paid to the fact that the oxidizing agent can provide the effect with a low

potassium nitrate content of 10 weight% or less of the total amount of gas generant composition. With a potassium nitrate content of more than 10 weight%, the outflow slag generated by the combustion of the gas generant composition increases. It is hard to filter out the slag originating from the

5 potassium through filters in the gas generator, so that there is the possibility that the slag may cause damage to the airbag or may scald the occupants. Also, if more potassium nitrate is used, it becomes hard to achieve the characteristic feature of the gas generant composition that the combustion speed is controlled moderately at the initial stage, so that there

10 is provided an increased possible fear of doing harm to the occupants.

When basic copper nitrate is added, the content of basic copper nitrate is preferably 30 weight% or less of the total amount of gas generant composition. It is possible to filter out the slag originating from the basic copper nitrate with ease, differently from the use of potassium nitrate, so

15 that a basic copper nitrate content of 30 weight% or less is permissible. If more basic copper nitrate is used, there is the possibility that the combustion speed of the gas generant composition may decrease so that a desired combustion speed cannot be obtained.

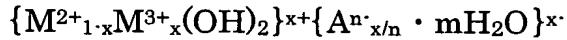
The additives that may be used include a slag forming agent and a

20 binder. In the gas generant composition of the present invention, silicon nitride or silicon carbide is preferably used as the slag forming agent. While silicon nitride and silicon carbide, which are called fine ceramics, are used as heat-resistant materials which are thermally stable and high resistant, they have the property of being decomposed in high temperature

oxidizing atmospheres. Through the use of this property, both processes of the slag forming and the gas generation are provided. The content of silicon nitride or silicon carbide is preferably in the range of 0.5 to 10 weight%. With a less than 0.5 weight% silicon nitride or silicon carbide, 5 the satisfactory effect cannot be expected in the slag collecting process. On the other hand, with a more than 10 weight% silicon nitride or silicon carbide, the content of fuel and oxidizing agent is decreased on the whole, so that there is the possibility of short amount of gas generated.

When fine particles of silicon nitride or silicon carbide are added in the 10 pulverizing process of the fuel or the oxidizing agent, they provide the effect of acting as an anti-caking agent. Silicon nitride or silicon carbide has the property of providing the slag forming capability without decreasing the combustion speed of the gas generant composition containing the low-energy fuel. If a required amount of SiO_2 is added as the slag forming agent, the 15 combustion speed is significantly decreased. Thus, the use of SiO_2 as the slag forming agent is not desirable for the present invention.

Further, hydrotalcites expressed by the following general formula are preferably used as the binder and slag forming agent:



20 where M^{2+} represents bivalent metals including Mg^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} ;

M^{3+} represents trivalent metals including Al^{3+} , Fe^{3+} , Cr^{3+} , Co^{3+} and In^{3+} ;

A^{n-} represents n-valence anions including OH^- , F^- , Cl^- , NO_3^- , CO_3^{2-} ,

SO₄²⁻, Fe(CN)₆³⁻, CH₃COO⁻, ion oxalate, and ion salicylate; and

$$X: 0 < x \leq 0.33.$$

Typical of the hydrotalcites are synthetic hydrotalcite expressed by the chemical formula of Mg₆Al₂(OH)₁₆CO₃ · 4H₂O or pyroaurite expressed by the

- 5 chemical formula of Mg₆Fe₂(OH)₁₆CO₃ · 4H₂O. The hydrotalcites, which are a porous material having water of crystallization, are very useful as a binder for a gas generant of nitrogen-containing organic compound. The gas generant composition containing the hydrotalcite as the binder can provide a degree of hardness much higher than a degree of hardness of a
10 pellet of a general type of azide base gas generant, particularly when used for the gas generant composition containing tetrazoles as the main component.

This seems to be because the hydrotalcites have the common property of being liable to absorb moisture, which property serves to firmly bind the

- 15 components of the gas generant. Also, the pellets using this binder keep their own characteristic and flammability characteristic unchanged against the thermal shock caused by temperature being raised and fallen repeatedly, thus enabling the pellets to be minimized in deterioration with age after practical installation on a vehicle. Further, it is probable that for example,
20 the synthetic hydrotalcite of the hydrotalcites is allowed to react as expressed by the following reaction formula (1) in the combustion of the gas generant.



Due to this, no harmful gas is produced. Also, the reaction itself is an

endothermic reaction, thus providing an advantageous effect of reducing the heat value of the gas generant. In addition, the decomposition product itself of the synthetic hydrotalcite forms spinel that can easily be filtered by the slag reaction of the acid base reaction expressed by the following

5 formula (2).



The content of the binder to the total gas generant composition is preferably in the range of 2 to 10 weight%. With the binder content of less than 2 weight%, the function as the binder is achieved with difficulty. On

10 the other hand, with the binder content of more than 10 weight%, the content of the fuel and oxidizing agent is decreased on the whole, so that there is the possibility of short amount of gas generated. Also, by adding the hydrotalcites to the gas generant composition, the gas generant composition is reduced in sensibility and, as a result of this, the effect of

15 providing an improved safety in the production process is also yielded.

Also, cellulosic binders or natural polymers may be used as the binder. These binders are suitable for the extrusion molding of the gas generant composition. To give an actual example of the cellulosic binders, at least one material selected from the group consisting of carboxymethyl cellulose, 20 methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, and hydroxylpropyl methyl cellulose can be cited. To give an actual example of the natural polymers, at least one material selected from the group consisting of Cyamoposis Gum or tragacanth gum can be cited. The content of the cellulosic binder or natural polymer is preferably in the range

of 2 to 10 weight%.

To give an actual example of other binders than the cellulosic binders, at least one material selected from the group consisting of polyacrylic acid, sodium polyacrylate, polyacrylamide, and two or three copolymerized compounds can be cited. The amount of those binders added is preferably in the range of 0.5 to 10 weight%. The addition of this binder provides the effect of providing an improved heat resistance of the gas generant composition.

Addition of silane compounds can provide an improved moldability in the extrusion molding process, in particular. The silane compounds that may be used include, for example, vinyltrimethoxysilane, vinyltriethoxysilane, vinyltris(β -methoxyethoxy)silane, β -(3,4-epoxycyclohexyl)ethyltrimethoxysilane, γ -glycidoxy propyltrimethoxysilane, γ -glycidoxy propylmethyl diethoxysilane, γ -methacryloxy propylmethyl dimethoxysilane, γ -methacryloxy propyltrimethoxysilane, γ -methacryloxy propyltriethoxysilane, N- β -(aminoethyl)- γ -aminopropylmethyl dimethoxysilane, N- β -(aminoethyl)- γ -aminopropyltrimethoxysilane, N- β -(aminoethyl)- γ -aminopropyltriethoxysilane, γ -aminopropyltrimethoxysilane, γ -aminopropyltriethoxysilane, N-phenyl- γ -aminopropyltrimethoxysilane, tetramethoxysilane, methyltrimethoxysilane, dimethyldimethoxysilane, phenyltrimethoxysilane, diphenyldimethoxysilane, tetraethoxysilane, methyltriethoxysilane, dimethyldiethoxysilane, phenyltriethoxysilane,

diphenyldiethoxysilane, hexyltrimethoxysilane, hexyltriethoxysilane, decyltrimethoxysilane, and hexamethyldisilazane. The amount of the silane compounds added is preferably in the range of 0.5 to 10 weight%.

Next, reference is given to a preferable combination of components of
5 the gas generant composition of the present invention. A preferable
combination of components of the gas generant composition is the
combination of 5-aminotetrazole and guanidine nitrate used as the fuel,
strontium nitrate used as the oxidizing agent, silicon nitride used as the
slag forming agent, and synthetic hydrotalcite used as the binder. This gas
10 generant composition preferably contains 10-30 weight% of 5-aminotetrazole,
5-30 weight% of guanidine nitrate, 30-70 weight% of strontium nitrate,
0.5-10 weight% of silicon nitride, and 2-10 weight% of synthetic hydrotalcite.
Further, in order to produce an increased combustion speed, it is preferable
that not more than 10 weight% of potassium nitrate or not more than 30
15 weight% of basic copper nitrate is contained. Guanidine nitrate is low in
energy, so that it has the tendency to cause the combustion speed to
decrease as the guanidine nitrate content increases. In addition, particles
of the guanidine nitrate are so hard that they cannot be pulverized with
ease. Although the particles of the guanidine nitrate of $50\mu\text{m}$ or more in
20 50% average particle diameter are easily obtained by use of a generally used
pin mill or ball mill as pulverizing means used in the manufacture of the
gas generant, since it is very difficult to pulverize the particles of the
guanidine nitrate into $40\mu\text{m}$ or less, particularly $20\mu\text{m}$ or less, a special
milling machine, such as a jet mill, must be used therefor. It is preferable

that silicon nitride is used as the slag forming agent. The addition of silicon nitride can provide good slag collecting properties without decreasing the combustion speed. Also, synthetic hydrotalcite should preferably be used as the binder in that it can provide not only improved hardness of the

5 gas generant composition but also reduced heat release value and improved slag collecting capabilities.

Another preferable combination of components of the gas generant composition is the combination of nitroguanidine and guanidine used as the fuel, strontium nitrate used as the oxidizing agent, silicon nitride used as

10 the slag forming agent, and a cellulosic binder used as the binder. This gas generant composition preferably contains 20-55 weight% of nitroguanidine, 5-30 weight% of guanidine nitrate, 30-60 weight% of strontium nitrate, 0.5-10 weight% of silicon nitride, and 2-10 weight% of celluloisc binder or synthetic hydrotalcite. Further, in order to produce an increased

15 combustion speed, it is preferable that not more than 10 weight% of potassium nitrate or not more than 30 weight% of basic copper nitrate is contained. The gas generant composition of the present invention containing nitroguanidine and guanidine nitrate as the fuel is preferably produced in the form of the gas generant by extrusion molding. The

20 cellulosic binder is particularly better for that formation. Any particular limitation is imposed on the kinds of binder, as long as they exhibit a proper degree of viscosity as a water soluble solvent. However, in the case of the oxidizing agent containing a phase stabilized ammonium nitrate, if it is used in combination with an anionic binder, an ionic reaction is produced to

cause the heat resistance to be significantly reduced, for the reason of which that combination is undesirable. In this case, a nonionic binder should preferably be used. It is preferable that silicon nitride is used as the slag forming agent. The addition of silicon nitride can provide good slag

- 5 collecting properties without decreasing the combustion speed.

Still another preferable combination of components of the gas generant composition of the present invention is the combination of 5-aminotetrazole and guanidine nitrate used as the fuel, strontium nitrate and ammonium perchlorate used as the oxidizing agent, polyacrylamido used as the binder,

- 10 and a silane compound used for the purpose of improving moldability at the extrusion molding. This gas generant composition preferably contains 10-30 weight% of 5-aminotetrazole, 5-30 weight% of guanidine nitrate, 10-50 weight% of strontium nitrate, 10-50 weight% of ammonium perchlorate, 0.5-10 weight% of polyacrylamido, and 0.5-10 weight% of silane
- 15 compound. It is preferable to add water as the solvent in the extrusion molding process. Preferably, silane compound having the property of being soluble in water is then used.

The gas generant composition of the present invention may selectively be formed into a granulated form, a granular form or a pellet form. Also,

- 20 the mixed conditioner may be formed in the press molding or extrusion molding. It may selectively be formed into a pellet form, a single-hole or a multi-hole (porous) tubular form, for example.

Then, reference will be given to the manufacturing method of the gas generant composition. The gas generant composition of the present

invention can be manufactured in either method of the press molding and the extrusion molding. After having been molded, the gas generant composition is heat-treated to be fully dried out, so as to prevent an ignition lag caused by the moisture and provide an improved environmental

5 resistance.

When the gas generant composition is molded by the press molding, the anti-caking agent is added to the fuel components and the oxidizing agent, first. Then, the respective components are mixed with a V-type blending machine and then are pulverized. After a prescribed quantity of

10 pulverized fuel components, pulverized oxidizing agent and auxiliary agent for molding are taken by measurement, they are mixed equally with the V-type blending machine. Thereafter, they are put into the press molding machine and then heat-treated. The gas generating molded products thus obtained are used as the gas generant composition.

15 Likewise, when the gas generant composition is molded by the extrusion molding, the fuel components and the oxidizing agent are pulverized, first. Then, after the respective components are taken by measurement and 8-25 weight% water in outer percentage is added thereto, they are fully kneaded to produce moist agents having viscosity. Thereafter,

20 they are formed into a desired form and cut properly by use of a vacuum kneading extrusion machine and then are subjected to heat treatment. The gas generating molded products thus obtained are used as the gas generant composition.

The present invention will be further detailed with reference to the

examples.

[Example 1]

24.7 parts by weight of 5-aminotetrazole (15 μm in 50% particle diameter) and 11.9 parts by weight of guanidine nitrate (30 μm in 50% particle diameter) used as the fuel, 53.4 parts by weight of strontium nitrate (13 μm in 50% particle diameter) used as the oxidizing agent, 5.0 parts by weight of silicon nitride (5 μm in 50% particle diameter) used as the slag forming agent, and 5.0 parts by weight of synthetic hydrotalcite (10 μm in 50% particle diameter) used as the binder were dry blended by use of the 5 V-type blending machine. Then, 15 parts by weight of water to the total quantity of mixed powders was sprayed on the powders under stirring. Thereafter, they were subjected to the wet granulation process to produce 10 granulated powders of not more than 1mm in particle diameter. After the granulated powders thus produced were dried by heating, they were pressed 15 into shapes by a rotary pelletizing machine to produce pellets of 5mm in diameter and 1.5mm in height of the gas generant composition of the present invention.

40g of pellets thus produced were packed in the gas generator 1 shown in FIG. 1. The gas generator 1 comprises a central igniting 20 chamber 7 in which an igniter 2 and a transfer charge 3 are arranged, a combustion chamber 8 which is located around the central igniting chamber and in which gas generants 4 are packed, and a cooling/filtering chamber 9 which is located around the combustion chamber and in which a woven metal wire 5 is disposed. The combustion gas is exhausted out from gas

exhausting holes 6 through the cooling/filtering chamber 9. After having been mounted to a container having an internal volume of 60 liter, the gas generator 1 was operated to discharge the gas into the container, whereby the change of pressure in container with time was measured. The 60 liter
5 tank test results are shown in TABLE 1 of FIG. 3.

[Example 2]

19.7 parts by weight of 5-aminotetrazole (15 μ m in 50% particle diameter) and 19.7 parts by weight of guanidine nitrate (10 μ m in 50% particle diameter) used as the fuel, 50.6 parts by weight of strontium nitrate
10 (13 μ m in 50% particle diameter) used as the oxidizing agent, 5.0 parts by weight of silicon nitride (5 μ m in 50% particle diameter) used as the slag forming agent, and 5.0 parts by weight of synthetic hydrotalcite (10 μ m in 50% particle diameter) used as the binder were dry blended by use of the V-type blending machine. Then, 15 weight% of water to the total quantity
15 of mixed powders was sprayed on the powders under stirring. Thereafter, they were subjected to the wet granulation process to produce granulated powders of not more than 1mm in particle diameter. After the granulated powders thus produced were dried by heating, they were pressed into shapes by the rotary pelletizing machine to produce pellets of 5mm in
20 diameter and 1.5mm in height of the gas generant composition of the present invention.

40g of pellets thus produced were packed in the gas generator 1 shown in FIG. 1 and the same test as that of Example 1 was performed. The results obtained are shown in the graph of FIG. 2 and TABLE 1 of FIG.

3. In the graph of FIG. 2, the result of this Example is indicated by a line
a.

[Example 3]

19.4 parts by weight of 5-aminotetrazole ($15\text{ }\mu\text{m}$ in 50% particle
5 diameter) and 19.4 parts by weight of guanidine nitrate ($10\text{ }\mu\text{m}$ in 50%
particle diameter) used as the fuel, 44.2 parts by weight of strontium nitrate
($13\text{ }\mu\text{m}$ in 50% particle diameter) and 7.0 parts by weight of potassium
nitrate ($35\text{ }\mu\text{m}$ in 50% particle diameter) used as the oxidizing agent, 5.0
parts by weight of silicon nitride ($5\text{ }\mu\text{m}$ in 50% particle diameter) used as
10 the slag forming agent, and 5.0 parts by weight of synthetic hydrotalcite
($10\text{ }\mu\text{m}$ in 50% particle diameter) used as the binder were dry blended by
use of the V-type blending machine. Then, 15 weight% of water to the total
quantity of mixed powders was sprayed on the powders under stirring.
Thereafter, they were subjected to the wet granulation process to produce
15 granulated powders of not more than 1mm in particle diameter. After the
granulated powders thus produced were dried by heating, they were pressed
into shapes by the rotary pelletizing machine to produce pellets of 6mm in
diameter and 1.5mm in height of the gas generant composition of the
present invention.
20 40g of pellets thus produced were packed in the gas generator 1
shown in FIG. 1 and the same test as that of Example 1 was performed.
The results obtained are shown in TABLE 1 of FIG. 3.

[Example 4]

41.5 parts by weight of nitroguanidine ($20\text{ }\mu\text{m}$ in 50% particle

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- diameter) and 8.2 parts by weight of guanidine nitrate ($10\mu\text{m}$ in 50% particle diameter) used as the fuel, 35.3 parts by weight of strontium nitrate ($13\mu\text{m}$ in 50% particle diameter) and 5.0 parts by weight of potassium nitrate ($35\mu\text{m}$ in 50% particle diameter) used as the oxidizing agent, 5.0
- 5 parts by weight of silicon nitride ($5\mu\text{m}$ in 50% particle diameter) used as the slag forming agent, and 5.0 parts by weight of synthetic hydrotalcite ($10\mu\text{m}$ in 50% particle diameter) used as the binder were dry blended by use of the V-type blending machine. Then, 15 weight% of water to the total quantity of mixed powders was sprayed on the powders under stirring.
- 10 Thereafter, they were subjected to the wet granulation process to produce granulated powders of not more than 1mm in particle diameter. After the granulated powders thus produced were dried by heating, they were pressed into shapes by the rotary pelletizing machine to produce pellets of 5mm in diameter and 2.0mm in height of the gas generant composition of the
- 15 present invention.

35g of pellets thus produced were packed in the gas generator 1 shown in FIG. 1 and the same test as that of Example 1 was performed. The results obtained are shown in TABLE 1 of FIG. 3.

[Example 5]

- 20 42.1 parts by weight of nitroguanidine ($20\mu\text{m}$ in 50% particle diameter) and 8.7 parts by weight of guanidine nitrate ($30\mu\text{m}$ in 50% particle diameter) used as the fuel, 39.2 parts by weight of strontium nitrate ($13\mu\text{m}$ in 50% particle diameter) used as the oxidizing agent, 5.0 parts by weight of silicon nitride ($5\mu\text{m}$ in 50% particle diameter) used as the slag

forming agent, and 5.0 parts by weight of methyl cellulose used as the binder were dry blended by use of the V-type blending machine. Then, 15 weight% of water to the total quantity of mixed powders was sprayed on the powders under stirring. Thereafter, they were vacuum deaerated while

- 5 being kneaded by use of a kneader. The clayey gas generant composition thus obtained was molded into shapes by use of a screw extrusion machine and then was dried by heating to thereby produce columnar molded products of gas generant composition of 3mm in diameter and 2mm in height.

- 10 35g of molded products thus produced were packed in the gas generator 1 shown in FIG. 1 and the same test as that of Example 1 was performed. The results obtained are shown in the graph of FIG. 2 and TABLE 1 of FIG. 3. In the graph of FIG. 2, the result of this Example is indicated by a line b.

15 [Example 6]

- 34.7 parts by weight of nitroguanidine ($20\mu\text{m}$ in 50% particle diameter) and 9.5 parts by weight of guanidine nitrate ($10\mu\text{m}$ in 50% particle diameter) used as the fuel, 36.8 parts by weight of strontium nitrate ($13\mu\text{m}$ in 50% particle diameter) and 10.5 parts by weight of basic copper nitrate ($11\mu\text{m}$ in 50% particle diameter) used as the oxidizing agent, 3.5 parts by weight of silicon nitride ($5\mu\text{m}$ in 50% particle diameter) used as the slag forming agent, and 5.0 parts by weight of methyl cellulose used as the binder were dry blended by use of the V-type blending machine. Then, 15 weight% of water to the total quantity of mixed powders was sprayed on

the powders under stirring. Thereafter, they were vacuum deaerated while being kneaded by use of the kneader. The clayey gas generant composition thus obtained was molded into shapes by use of the screw extrusion machine and then was dried by heating to thereby produce columnar

- 5 molded products of gas generant composition of 4mm in diameter and 2mm in height.

35g of molded products thus produced were packed in the gas generator 1 shown in FIG. 1 and the same test as that of Example 1 was performed. The results obtained are shown in TABLE 1 of FIG. 3.

10 [Comparative Example 1]

30.9 parts by weight of 5-aminotetrazole (15 μ m in 50% particle diameter) used as the fuel, 57.9 parts by weight of strontium nitrate (13 μ m in 50% particle diameter) used as the oxidizing agent, 5.0 parts by weight of silicon nitride (5 μ m in 50% particle diameter) used as the slag forming

- 15 agent, and 5.0 parts by weight of synthetic hydrotalcite (10 μ m in 50% particle diameter) used as the binder were dry blended by use of the V-type blending machine. Then, 15 parts by weight of water to the total quantity of mixed powders was sprayed on the powders under stirring. Thereafter, they were subjected to the wet granulation process to produce granulated
20 powders of not more than 1mm in particle diameter. After the granulated powders thus produced were dried by heating, they were pressed into shapes by the rotary pelletizing machine to produce pellets of gas generant composition of 5mm in diameter and 2.0mm in height.

40g of pellets thus produced were packed in the gas generator 1

shown in FIG. 1 and the same test as that of Example 1 was performed.

The results obtained are shown in the graph of FIG. 2 and TABLE 1 of FIG.

3. In the graph of FIG. 2, the result of this Comparative Example is indicated by a line c.

5 [Comparative Example 2]

50.6 parts by weight of guanidine nitrate ($15\text{ }\mu\text{m}$ in 50% particle diameter) used as the fuel, 39.4 parts by weight of strontium nitrate ($13\text{ }\mu\text{m}$ in 50% particle diameter) used as the oxidizing agent, 5.0 parts by weight of silicon nitride ($5\text{ }\mu\text{m}$ in 50% particle diameter) used as the slag forming

10 agent, and 5.0 parts by weight of synthetic hydrotalcite ($10\text{ }\mu\text{m}$ in 50% particle diameter) used as the binder were dry blended by use of the V-type blending machine. Then, 15 parts by weight of water to the total quantity of mixed powders was sprayed on the powders under stirring. Thereafter, they were subjected to the wet granulation process to produce granulated
15 powders of not more than 1mm in particle diameter. After the granulated powders thus produced were dried by heating, they were pressed into shapes by the rotary pelletizing machine to produce pellets of gas generant composition of 5mm in diameter and 1.5mm in height.

40g of pellets thus produced were packed in the gas generator 1
20 shown in FIG. 1 and the same test as that of Example 1 was performed.

The results obtained are shown in the graph of FIG. 2 and TABLE 1 of FIG.

3. In the graph of FIG. 2, the result of this Comparative Example is indicated by a line d.

[Comparative Example 3]

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E
- 24.7 parts by weight of 5-aminotetrazole ($15\mu\text{m}$ in 50% particle diameter) and 11.9 parts by weight of guanidine nitrate ($50\mu\text{m}$ in 50% particle diameter) used as the fuel, 53.4 parts by weight of strontium nitrate ($13\mu\text{m}$ in 50% particle diameter) used as the oxidizing agent, 5.0 parts by 5 weight of silicon nitride ($5\mu\text{m}$ in 50% particle diameter) used as the slag forming agent, and 5.0 parts by weight of synthetic hydrotalcite ($10\mu\text{m}$ in 50% particle diameter) used as the binder were dry blended by use of the V-type blending machine. Then, 15 parts by weight of water to the total quantity of mixed powders was sprayed on the powders under stirring.
- 10 Thereafter, they were subjected to the wet granulation process to produce granulated powders of not more than 1mm in particle diameter. After the granulated powders thus produced were dried by heating, they were pressed into shapes by the rotary pelletizing machine to produce pellets of gas generant composition of 5mm in diameter and 1.5mm in height.
- 15 40g of pellets thus produced were packed in the gas generator 1 shown in FIG. 1 and the same test as that of Example 1 was performed. The results obtained are shown in the graph of FIG. 2 and TABLE 1 of FIG. 3. In the graph of FIG. 2, the result of this Comparative Example is indicated by a line e.
- 20 As clearly seen from the results of FIGS. 2 and 3, in the 60 liter tank test, the molded products of the gas generant composition of Examples 1-6 of the present invention provide the results that the gas generating speed increases in a controlled rate in the period of 10-20ms from the ignition and then increases sharply on and after 20ms and the pressure becomes

substantially the same level as that of the conventional gas generant composition on and after 40ms. It is understood from this that the molded products of the gas generant composition of the present invention provided suitable burning performances for the gas generator.

- 5 In comparison with this, the gas generant composition of Comparative Example 1, in which guanidine nitrate is not added as the fuel, in other words, the fuel consists of only a high-energy nitrogen-containing organic compound, provides the result that the 60 liter tank pressure increases largely in the period of 20ms from the ignition, as seen from FIGS. 2 and 3,
- 10 and thus provides an increased harm for the inflator. The gas generant composition of Comparative Example 2, in which the fuel consists of only a low-energy guanidine nitrate, provides excessive reduction in combustion speed, as seen from FIG. 2, and thus is improper as the gas generant. The gas generant composition of Comparative Example 3 provides the result
- 15 that when the 50% average particle diameter of guanidine nitrate exceeds $40\mu\text{m}$, the 60 liter tank pressure becomes little more than that of Comparative Example 1 and does not provide the effects of the present invention.

- As clearly seen from the description above, in the gas generant
20 composition of the present invention, the fuel comprises at least two nitrogen-containing organic compounds comprising a high-energy nitrogen-containing organic compound exhibiting a high combustion speed and a low-energy nitrogen-containing organic compound exhibiting a low combustion speed, and the low-energy nitrogen-containing organic

compound is made to have the 50% average particle diameter of $40 \mu\text{m}$ or less, whereby the gas generant composition exhibiting a suitable burning behavior for the gas generator is provided. Thus, the gas generator having the combustion performance of doing little harm to the risers can be

5 realized with ease and at low cost by using the gas generant comprising the gas generant composition of the present invention.

Capabilities of Exploitation in Industry

The present invention provides an optimum gas generant composition useful for gas generants used for a gas generator for an automobile occupant

10 restraint system, such as an airbag and a pretensioner, which exhibits the burning characteristics to produce a further ideal occupant protecting performance, without any complex production process being required and without any limitation being imposed on the forms of the gas generants.

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